

AD-A149 813

AN INFRARED STUDY OF THE DISSOCIATION OF CARBON DIOXIDE  
OVER SUPPORTED RHODIUM CATALYSTS(U) AUBURN UNIV AL DEPT  
OF CHEMISTRY M A HENDERSON ET AL. 07 JAN 85 TR-2

1/1

UNCLASSIFIED

N00014-83-K-0637

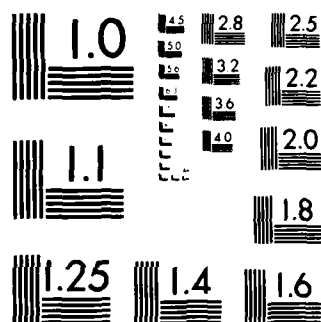
F/G 7/4

NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

SEC

AD-A149 813

## RT DOCUMENTATION PAGE

1a. <b>Unclassified</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		Unlimited	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 2		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Auburn University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research - Code 413	
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry (Dr. S. D. Worley) Auburn University, AL 36849		7b. ADDRESS (City, State and ZIP Code) 800 North Quincy St. Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (If applicable) Code 413	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0637	
8c. ADDRESS (City, State and ZIP Code) See 7b		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT NO.
11. TITLE (Include Security Classification) An Infrared Study of the Dissociation of Carbon Dioxide over Supported Rhodium Catalysts		NR634-844	
12. PERSONAL AUTHOR(S) M.A. Henderson and S. D. Worley			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day) 85 Jan. 7	15. PAGE COUNT 11
16. SUPPLEMENTARY NOTATION Accepted for publication by <u>Surface Science</u>			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
		Infrared Spectroscopy, Carbon Dioxide, Methanation, Supported Rhodium Catalysts.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) An infrared study has been performed concerning the possible dissociation of CO <sub>2</sub> on supported Rh catalyst films. The data indicate that CO <sub>2</sub> does dissociate on Rh/TiO <sub>2</sub> and Rh/Al <sub>2</sub> O <sub>3</sub> to form a carbonyl hydride species in accord with the work of Solymosi. This dissociation process is considerably enhanced by the presence of a small amount of hydrogen gas, but will proceed in the absence of hydrogen gas with the assistance of hydrogen migration from the support. Impurity boron also enhances the formation of the carbonyl hydride species, and hence CO <sub>2</sub> dissociation, when it is present in the supported Rh films.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified <b>A</b>	
22a. NAME OF RESPONSIBLE INDIVIDUAL S. D. Worley		22b. TELEPHONE NUMBER (Include Area Code) 205-826-4043	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR

EDITION OF 1 JAN 73 IS OBSOLETE.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

85 01 08 054

**CONTRACT N00014-83-K-0637**

## TECHNICAL REPORT NO. 2

**by**

**Prepared for Publication**

## Surface Science

System For  
 CR&I ☒  
 TAB ☐  
 announced ☐  
 location

This document has been approved for public release and sale; its distribution is unlimited.

85 01 08 054

An Infrared Study of The Dissociation of Carbon Dioxide over Supported  
Rhodium Catalysts

M. A. Henderson and S. D. Worley\*

Department of Chemistry, Auburn University, Auburn University, AL 36849

ABSTRACT

An infrared study has been performed concerning the possible dissociation of  $\text{CO}_2$  on supported Rh catalyst films. The data indicate that  $\text{CO}_2$  does dissociate on Rh/ $\text{TiO}_2$  and Rh/ $\text{Al}_2\text{O}_3$  to form a carbonyl hydride species in accord with the work of Solymosi. This dissociation process is considerably enhanced by the presence of a small amount of hydrogen gas, but will proceed in the absence of hydrogen gas with the assistance of hydrogen migration from the support. Impurity boron also enhances the formation of the carbonyl hydride species, and hence  $\text{CO}_2$  dissociation, when it is present in the supported Rh films.

\*Author to whom correspondence should be addressed.

The dissociation of carbon dioxide on rhodium, or lack thereof, has become a very controversial topic, but one of great importance in methanation chemistry. Somorjai and coworkers have reported that  $\text{CO}_2$  does dissociate on Rh foil and on several different Rh single crystal surfaces with high probability (ca.  $10^{-1}$ ) even at 300 K [1-5]. In those studies a variety of surface-sensitive techniques (TDS, LEED, and HREELS) were employed. However, Weinberg has recently questioned the results of Somorjai and coworkers based upon calculations employing available thermodynamic and kinetic data including an activation energy for the dissociation of  $\text{CO}_2$  on clean Rh of 20.6 kcal/mol. He has suggested that the probability of dissociative adsorption of  $\text{CO}_2$  on Rh is only  $10^{-15}$  at low pressure and ambient temperature [6]. Somorjai [7] has rebutted the arguments of Weinberg by reviewing numerous literature references suggestive of  $\text{CO}_2$  dissociation on Rh [8] and by using a corrected activation energy for the  $\text{CO}/\text{O}$  associative reaction on Rh [9] which entailed the use of an activation energy for dissociation of  $\text{CO}_2$  on Rh of only 8.1 kcal/mol in his calculations and thus predicts a much higher probability of dissociation at 300 K than  $10^{-15}$ . However Goodman and coworkers [10] have recently measured the activation energy for  $\text{CO}_2$  dissociation on Rh(111) to be 17 kcal/mol and concluded that the probability of the dissociation process on Rh at 300 K and 760 Torr is only  $10^{-11}$ . Very recently Solymosi and Kiss [11] have studied the adsorption and dissociation of  $\text{CO}_2$  on Rh(111) and Rh foil using Auger, EELS, and TDS; they could find no evidence of  $\text{CO}_2$  dissociation on clean Rh at 300 K. They did find dissociative chemisorption of  $\text{CO}_2$  on Rh at 300 K when either  $\text{H}_2$  or impurity boron was present [11]. The purpose of this letter is to report recent infrared findings from these laboratories concerning the dissociation of  $\text{CO}_2$  on supported Rh catalysts as a part of an extensive study of  $\text{CO}_2$  methanation.

The supported Rh catalysts used in this study were prepared as thin films on  $\text{CaF}_2$  infrared windows by techniques employed here previously for infrared work involving CO adsorption on supported Rh [12-14] and the hydrogenation of CO over supported Rh [15]. For all of the work described here the Rh precursor salt was  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ . The support materials were alumina (Degussa Aluminum Oxide C,  $100 \text{ m}^2\text{g}^{-1}$ ) and titania (Degussa Titanium Dioxide P25,  $50 \text{ m}^2\text{g}^{-1}$ ). The gases employed ( $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{CO}_2$ ) were of the highest purity obtainable from Matheson; the  $\text{H}_2$  and  $\text{D}_2$  were passed through liquid nitrogen traps before use. A Pyrex infrared cell similar to the one used here has been described previously [12-15]. All spectra were accumulated by a Perkin-Elmer 983 spectrometer operated at a resolution of  $4.5 \text{ cm}^{-1}$  at  $2000 \text{ cm}^{-1}$ . A Perkin-Elmer infrared data station facilitated data processing and storage.

Figure 1 shows the infrared spectra resulting from various sequential treatments of a 10% by weight Rh/ $\text{TiO}_2$  film. The sample was heated to 460 K at  $2 \times 10^{-6}$  Torr for one hr and then reduced at 470 K by four successive doses of hydrogen at 70 Torr for time intervals of 5, 5, 10 and 20 min, each reduction cycle being followed by evacuation to  $10^{-5}$  Torr. Then the sample was heated at 523 K for 16 hr at  $2 \times 10^{-6}$  Torr to remove as much hydrogen from the support as possible (complete removal is not possible at 523 K). A 12.6 Torr dose of  $\text{CO}_2$  was then introduced into the infrared cell at 298 K and spectrum a in Fig. 1 was recorded immediately thereafter. Under these conditions no bands in the  $2000 \text{ cm}^{-1}$  region indicative of  $\text{CO}_2$  dissociation to adsorbed CO species are evident. The bands at 1670, 1604, 1435, and  $1221 \text{ cm}^{-1}$  are indicative of the formation of carbonate and/or bicarbonate species on the support [16]. The sample was heated at 503 K for 4 hr; spectrum 1b was recorded after 30 min at 503 K, and spectrum 1c after the 4 hr heating period. A weak band developed near  $2030 \text{ cm}^{-1}$  during this heating cycle indicating the dissociation of  $\text{CO}_2$  to some type of adsorbed

CO species. Then the sample cell was cooled to 298 K, evacuated, and dosed with 13 Torr of a 20:1 mixture of CO<sub>2</sub> and H<sub>2</sub>. Spectrum 1d was immediately recorded at 298 K. Obviously the dissociation process is enhanced by the presence of the hydrogen gas as the 2032 cm<sup>-1</sup> band doubles in intensity rapidly without heating. Spectrum 1e was recorded after only 30 min of heating at 503 K. The large intensity enhancement and shift to higher wavenumber (2038 cm<sup>-1</sup>) of the CO band are indicative of increased coverage of the CO species on the Rh/TiO<sub>2</sub> surface, and hence to enhanced dissociation of CO<sub>2</sub> caused by the presence of H<sub>2</sub>. A small band near 1893 cm<sup>-1</sup> in spectrum 1e can be attributed to a bridged carbonyl species, either between two Rh atoms, or between a Rh atom and the support [12-15].

Experiments employing boric acid as a dopant were also conducted, typical spectral data being shown in Fig. 2. In these experiments ca. 4.9% by weight H<sub>3</sub>BO<sub>3</sub> was added to the 10% Rh/TiO<sub>2</sub> sample slurry, and the mixture was sprayed onto a CaF<sub>2</sub> window in the usual fashion. The sample was subjected to the same reduction and heating process as used for the experiment discussed earlier (Fig. 1). Spectra a, b, and c in Fig. 2 have been reproduced from Fig. 1 for comparison. Spectrum 2d refers to the doped sample exposed to 12.9 Torr of CO<sub>2</sub> at 298 K. There are no bands in 2d which can be attributed to an adsorbed CO species; large new bands in the 1200-1500 cm<sup>-1</sup> region must correspond to the reduced H<sub>3</sub>BO<sub>3</sub> interacting in an undefined, complex manner with the support and possibly with the Rh. However, the important spectral development occurs upon heating to 503 K. The CO species having its band at 2030-2040 cm<sup>-1</sup> again grows with time, and obviously at a greater rate than was the case for the undoped sample (spectra a, b, and c). Thus it would appear that the presence of the impurity boron species does enhance the dissociation of CO<sub>2</sub> over Rh/TiO<sub>2</sub> also, although not to as great an extent as does H<sub>2</sub>. It should be noted that similar observations have been found here for 10% Rh/Al<sub>2</sub>O<sub>3</sub> in the



presence of  $H_2$  and  $H_3BO_3$ ; however, the enhancement of  $CO_2$  dissociation is more evident when  $TiO_2$  is the support than for  $Al_2O_3$ .

Solymosi and coworkers have previously observed that  $H_2$  enhances the dissociation of  $CO_2$  over supported Rh catalysts [16]. They have also suggested that a carbonyl hydride may well be the species giving rise to the



low frequency CO band which they observed for Rh/ $Al_2O_3$  at  $2020-2039\text{ cm}^{-1}$ . We have also suggested that the carbonyl hydride species is an intermediate in the methanation of CO [15]. On the other hand, Iizuka and Tanaka [17] have concluded that this band is merely due to a linearly bound CO species at low coverage because they observed the same frequency with or without the presence of  $H_2$ . We agree strongly with the Solymosi interpretation. We have repeated the experiments discussed here using  $CO_2$  and  $D_2$ . We obtain bands in the  $2020-2040\text{ cm}^{-1}$  region of the same intensities under analogous conditions, but at lower frequencies by ca.  $10\text{ cm}^{-1}$ , when  $D_2$  is employed. This is consistent with a carbonyl deuteride species in that the isotopic substitution is two bonds removed from the CO moiety. The low frequency shift can not be attributed to lower CO coverage because the CO bands for the two experiments have the same intensity. One might wonder from where the carbonyl hydride arises which causes the weak band in spectra 1b and 1c given that no hydrogen gas was present in these experiments. We believe that the source of this hydrogen is the support material. Heating at 523 K and  $2 \times 10^{-6}$  Torr for 16 hr is just not sufficient to remove all hydrogen from the support. We have demonstrated this by producing  $HCD_3$  and  $CH_2D_2$ , as well as  $CD_4$ , from a heated  $CO_2/D_2$

mixture over Rh/TiO<sub>2</sub> pretreated by reduction in D<sub>2</sub>[18]. The only possible source of H in this experiment was an "inverse spillover effect" from the support material. In other words, hydrogen migrates from the support to Rh to form the carbonyl hydride species. This process is more pronounced when TiO<sub>2</sub> is the support relative to Al<sub>2</sub>O<sub>3</sub>.

Our experiments on supported Rh catalyst films have also supported the findings of Solymosi and Kiss[11] as regards the enhancement of CO<sub>2</sub> dissociation on Rh by impurity boron. They suggested that the formation of a B-O surface species due to the strength of a B-O bond (787 kJ/mol) is the driving force for the dissociation process. Our results showed an enhancement of the carbonyl hydride IR band when boric acid was present. This probably means an increase in CO coverage to form the carbonyl hydride species because of enhanced dissociation of the CO<sub>2</sub> caused by impurity boron.

Unfortunately our results do not allow us to predict or calculate the probability of dissociation of CO<sub>2</sub> on Rh to help resolve the current controversy [1-7]. However, we have observed a carbonyl hydride species by infrared which could only result from the dissociation of CO<sub>2</sub> on Rh. furthermore, this process is enhanced by the presence of impurity boron, and greatly enhanced by the presence of H<sub>2</sub> gas such that dissociation occurs at 298 K when small amounts of H<sub>2</sub> are present. We suspect that the presence of either impurities or hydrogen is probably necessary for significant dissociation of CO<sub>2</sub> on Rh at ambient temperature and moderate pressure (eg. 10 Torr) of CO<sub>2</sub>.

#### Acknowledgement

We gratefully acknowledge the support of the Office of Naval Research for this work. We also acknowledge stimulating conversations with F. Solymosi, D.W. Goodman, and J.M. White concerning the CO<sub>2</sub> dissociation

problem. We thank F. Solymosi for access to reference 11 in advance of publication.

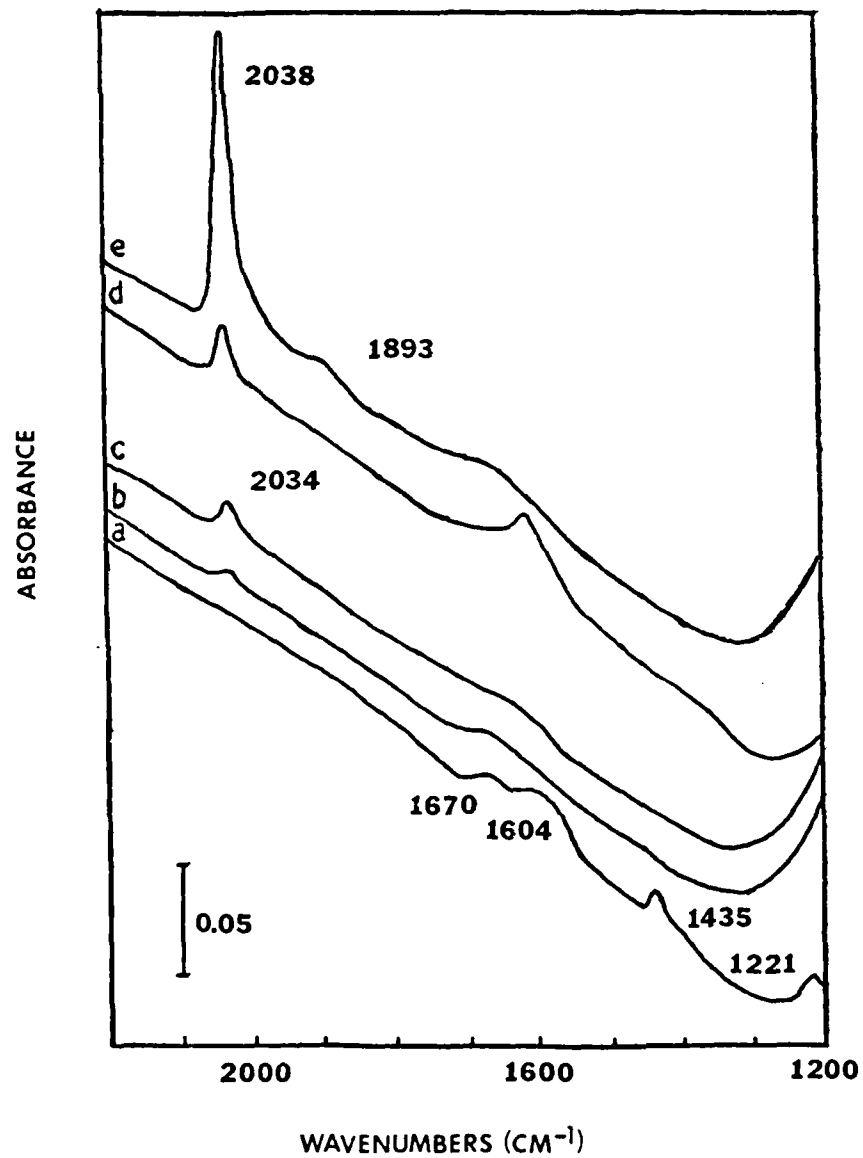
## References

- [1] B.A. Sexton and G.A. Somorjai, J. Catal. 46(1977)167.
- [2] D.G. Castner, B.A. Sexton, and G.A. Somorjai, Surface Sci. 71(1978)519.
- [3] D.G. Castner and G.A. Somorjai, Surface Sci. 83(1979)60.
- [4] L.H. Dubois and G.A. Somorjai, Surface Sci. 88(1979)L13.
- [5] L.H. Dubois and G.A. Somorjai, Surface Sci. 91(1980)514.
- [6] W.H. Weinberg, Surface Sci. 128(1983)L224.
- [7] L.H. Dubois and G.A. Somorjai, Surface Sci. 128(1983)L231.
- [8] See the numerous references quoted in reference 7.
- [9] C.T. Campbell, S.K. Shi, and J.M. White, Appl. Surface Sci. 2(1979)382; J. Vac. Sci. Tech. 16(1979)605; J. Phys. Chem. 83(1979)2255.
- [10] D.W. Goodman, D.E. Peebles, and J.M. White, Surface Sci. 140(1984)L239.
- [11] F. Solymosi and J. Kiss, Surface Sci., in press.
- [12] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin, and A.R. Tarrer, J. Chem. Phys. 74(1981)6487.
- [13] S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin, and A. R. Tarrer, J. Chem. Phys. 76(1982)20.
- [14] S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin, and A.R. Tarrer, J. Phys. Chem. 86(1982)2714.
- [15] S.D. Worley, G.A. Mattson, and R. Caudill, J. Phys. Chem. 87(1983)1671.
- [16] F. Solymosi, A. Erdohelyi, and M. Kocsis, J. Catal. 65(1980)428; F. Solymosi, E. Erdohelyi, and T. Bansagi, J. Catal. 68(1981)371; F. Solymosi, A. Erdohelyi and T. Bansagi, J. Chem. Soc. Faraday Trans. 1 77(1981)2645; A. Erdohelyi, M. Kocsis, T. Bansagi, and F. Solymosi, Acta Chim. Acad. Scien. Hung. Tomus 111(1982)591.
- [17] T. Iizuka and Y. Tanaka, J. Catal. 70(1981)449; T. Iizuka, Y. Tanaka, and K. Tanabe, J. Catal. 76(1982)1.
- [18] M. H. Henderson and S. D. Worley, to be published in due course.

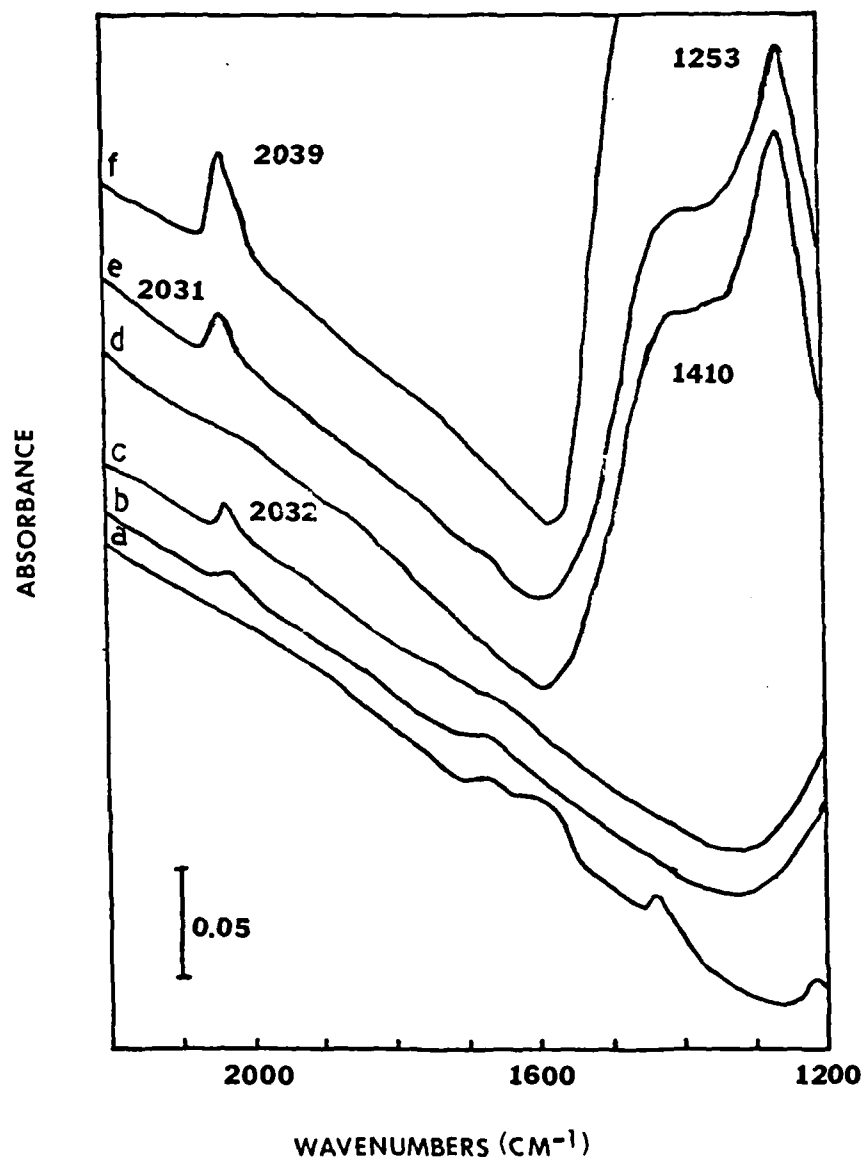
### Figure Captions

Fig. 1 Infrared spectra of a 10% Rh/TiO<sub>2</sub> film (4.1 mg/cm<sup>2</sup>) following reduction at 470 K, heating at 523 K for 16 hr at 2x10<sup>-6</sup> Torr, and then: (a) introduction of 12.6 Torr CO<sub>2</sub> at 298 K, (b) heating at 503 K for 30 min, (c) heating at 503 K for 4 hr, (d) cooling to 298 K, evacuation, and introduction of 13.1 Torr of a 20:1 mixture of CO<sub>2</sub>: H<sub>2</sub>, (e) heating at 503 K for 30 min.

Fig. 2. Infrared spectra of a 10% Rh/TiO<sub>2</sub> film (4.5 mg/cm<sup>2</sup>) doped with 4.9% H<sub>3</sub>BO<sub>3</sub> following reduction at 470 K, heating at 523 K for 17.75 hr at 2x10<sup>-6</sup> Torr, and then: (d) introduction of 12.9 Torr CO<sub>2</sub> at 298 K, (e) heating at 503 K for 30 min, (f) heating at 503 K for 4 hr. Spectra (a)-(c) are those shown in Fig. 1 for a film free of H<sub>3</sub>BO<sub>3</sub>.



Anderson, M. J. et al., 1971



*Henderson et al. 1971*

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		



ABSTRACTS DISTRIBUTION LIST, 634

Dr. K. N. Nicholas  
Department of Chemistry  
University of Oklahoma  
Norman, Oklahoma 73019

Dr. Aaron Fletcher  
Code 3852  
Naval Weapons Center  
China Lake, California 93555

Dr. A. Wold  
Department of Chemistry  
Brown University  
Providence, Rhode Island 02912

Dr. J. Cooper  
Code 6130  
Naval Research Laboratory  
Washington, D.C. 20375

Dr. M. C. Baird  
Department of Chemistry  
Queen's University  
Kingston, Canada  
K7L 3N6

Dr. N. N. Lichtin  
Department of Chemistry  
Boston University  
685 Commonwealth Avenue  
Boston, Massachusetts 02215

Dr. R. Eisenberg  
Department of Chemistry  
University of Rochester  
Rochester, New York 14627

Dr. N. Cooper  
Department of Chemistry  
Harvard University  
Cambridge, Massachusetts 02138

Dr. S. D. Worley  
~~Department of Chemistry~~  
~~Auburn University~~  
~~Auburn, Alabama 36830~~

Dr. L. Vaska  
Department of Chemistry  
Clarkson College  
Potsdam, New York 13676

Dr. R. A. Huggins  
Materials Science and  
Engineering Department  
Stanford University  
Stanford, California 94305

**END**

**FILMED**

**2-85**

**DTIC**